



## Memorandum

*To: Daniel Peabody*

*From: Scott Kirchner, CHMM*

*Date: November 28, 2018*

*Subject: Summary of Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site, Operable Unit 5, Area 1 Polychlorinated Biphenyl Congener and Aroclor Split Soil Samples*

### Introduction

This memorandum summarizes polychlorinated biphenyl (PCB) congener and Aroclor results from the Michigan Department of Environmental Quality's (MDEQ's) split soil sampling for Operable Unit 5 (OU-5) Area 1 of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site (site). These samples were collected during the OU-5 Area 1 pre-design sampling event performed June 19 through 27, 2018.

During the 2018 soil sampling event, Wood Environment & Infrastructure Solutions, Inc. (Wood) personnel collected multiple soil samples. Wood personnel homogenized and split with MDEQ twenty-two of these soil samples and one field duplicate. MDEQ accepted two aliquots of each split sample, one for Aroclor analysis and one that was held by its analytical laboratory for potential PCB congener analysis. Wood's split soil samples were sent to Pace Analytical Services, LLC (Pace) of Green Bay, Washington for Aroclor extraction and analysis. MDEQ sent all of its aliquots to Integrated Analytical Laboratories, LLC (IAL) of Randolph, New Jersey, with the first set of twenty-two soil splits subjected to Aroclor extraction and analysis. Following IAL's Aroclor analyses, CDM Smith personnel selected twelve of the split sample aliquots to be sent by IAL to Vista Analytical Laboratory (Vista) of El Dorado Hills, California. Vista performed PCB congener extraction and analysis on these twelve split samples.

CDM Smith also submitted three certified reference material (CRM) samples to IAL to examine the laboratory's ability to identify and recover the known Aroclor concentration in the CRMs. CDM Smith also submitted a single CRM sample to Vista to be included in extraction and congener analysis. The extraction method used by Pace was EPA Method SW-846 3541 *Automated Soxhlet Extraction* (EPA, 1994). The extraction method used by IAL was EPA Method SW-846 3550c *Ultrasonic Extraction* (EPA, 2007). Both Pace and IAL labs utilized EPA Method 8082A *Polychlorinated Biphenyls (PCBs) by Gas Chromatography* (EPA, 2007a). Vista used EPA Method 1668, Revision A *Chlorinate Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS* for extraction and analysis of 209 PCB congeners (EPA, 1999).

CDM Smith provided a memorandum discussing the 2018 Aroclor split sample results and IAL's associated data report to MDEQ on October 15, 2018 (CDM Smith, 2018). Wood, Georgia-Pacific, and International Paper subsequently requested Environmental Standards, Inc (ES) from Valley Forge, PA review the data package provided by MDEQ's contract laboratory, IAL. ES's November 5, 2018 memorandum stated that although there were differences in the Pace and IAL extraction methods, the split data compared well as all split sample relative percent differences (RPDs) met the QAPP criteria of 100% and 15 samples met MDEQ's field duplicate criterion of 50% (Environmental Standards, 2018).

Following receipt of IAL's Aroclor split sample results, MDEQ and CDM Smith directed IAL to send twelve of the split samples to Vista for congener analysis. The congener analyses were to be used to confirm that the reported total PCB Aroclor concentration results sufficiently represented total PCB concentrations present in the samples and, ultimately, at the site. The split sample results from both sets of Aroclor analyses (Pace and IAL) and PCB Congener analysis are presented below to advance the understanding of soil PCB concentration results in OU-5 Area 1 soils. A thirteenth split sample submitted for congener analysis may have been treated as a matrix spike and therefore is not being included as part of this evaluation.

### **Literature Summary of Aroclor versus Congener PCB Analysis**

Ecological risk assessment has historically utilized Aroclor analysis for assessment of PCB contamination in environmental media. Aroclors are multi-component mixtures, so analysis of individual Aroclors in environmental media requires matching a sample's individual Aroclor patterns to those of the Aroclor standards used during the analysis (Bernhard & Petron, 2001; Butcher, Gauthier, & Garvey, 1997; EPA, 2007). One of the main challenges encountered during Aroclor analyses is the potential inability to identify individual Aroclor patterns. This could be due to:

- presence of multiple Aroclors,
- significant temporal changes in Aroclor patterns arising from:
  - weathered PCBs,
  - degraded PCBs,
  - metabolized PCBs

(Bernhard & Petron, 2001; Butcher et al., 1997; Cleverly, 2003; EPA, 2007; Rushneck et al., 2004; Stalling, Schwartz, Dunn, & Wold, 1987).

The inability to accurately identify individual Aroclor patterns can lead to inadequate data on total PCB concentrations, exposure, and risks, and ultimately to less or non-effective risk-based soil remediation efforts. An alternative to Aroclor analysis is congener analysis, where 209 individual PCB compounds (also known as congeners) are analyzed. Congener analysis provides the ability to identify total PCB concentration regardless of the source congener mixture or its complexity. Although congener analysis is more costly than Aroclor analysis, congener analysis has lower quantification limits, is not subject to trying to identify individual Aroclor patterns, and can provide more direct measurements of risk due to PCB toxicity being congener based (Bernhard & Petron, 2001; Cleverly, 2003; Narquis, Prignano, & Hyatt, 2007).

### **Split Sample Finding**

MDEQ's split sample study was not designed to replicate Wood's analytical approach. The main objectives of MDEQ's soil split sampling for OU-5 Area 1 study were:

1. to confirm Wood's identification of site Aroclors using EPA Method 8082A,
2. to confirm Wood's reported concentration of total Aroclor PCB using EPA Method 8082A,
3. to evaluate if using EPA Method 8082A for total Aroclor results underrepresented total PCB concentrations at the site by comparison to total PCB by congener results using EPA Method 1668A.

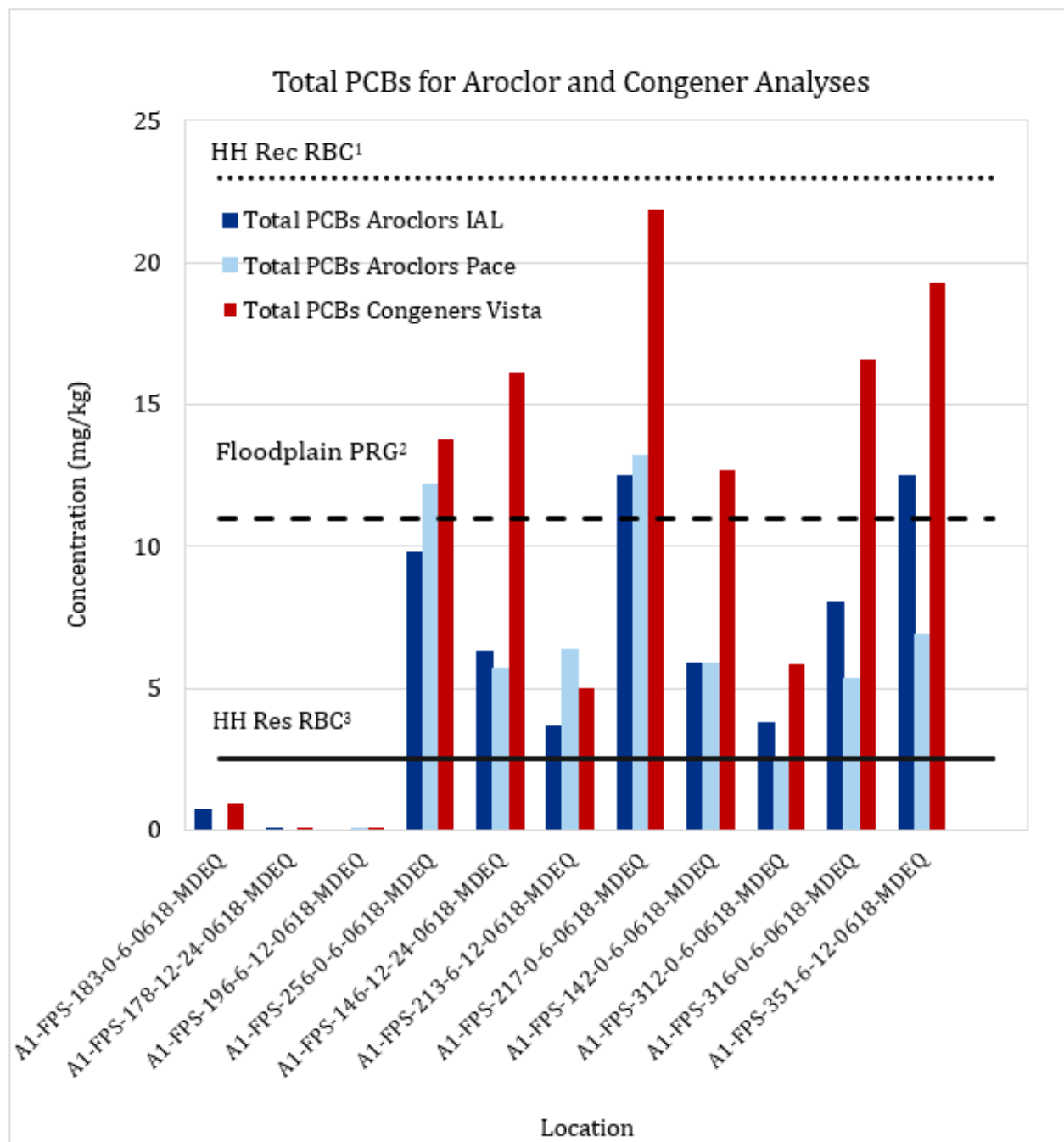
Three sets of data are used in this evaluation:

1. Aroclor analysis under method 8082A performed by Pace following their analytical SOPs,
2. Aroclor analysis under method 8082A performed by IAL following their analytical SOPs,
3. congener analysis under method 1668A performed by Vista following their analytical SOPs.

### ***Total PCBs***

The soil results presented below are compared based on the total PCB concentrations reported by the analytical laboratories. This number is a sum of all individual concentrations detected, either as Aroclors or congeners detected. The IAL data included two additional Aroclors compared to Pace (Aroclors 1262 and 1268); however, the results for these two additional Aroclors were excluded when calculating total PCB concentration present to better directly compare the lab results as performed under method 8082A. As seen on **Figure 1** below, total PCBs for Aroclor analysis from both labs seem to be comparable. Results from IAL have a slightly higher bias as compared to Pace results, with 54.5% of comparable locations trending higher in total Aroclor PCB concentrations reported from IAL (when the two additional Aroclors are removed). Total PCB by Aroclor analyses seem to be biasing low as compared to congener analysis as 90% of comparable locations have higher total PCB as congener concentration.

The calculated CRM IAL recovery average based on the three CRM PCB in soil samples analyzed was 57.3% with standard deviation of 10.2%, as seen below in the **Figure 2**. The CRM recovery from Congener analysis was 75.2%, and there was a 38% higher CRM recovery for congener vs Aroclor analysis (3.69 vs 2.29 mg/kg, respectively). It is important to note that the all CRM recoveries achieved by IAL and Vista laboratories were within the QC performance acceptance limits identified on the ERA certificates of analysis (CDM Smith, 2018). Both Aroclor and congener recoveries indicate potentially low bias of PCB results. The low bias of IAL's Aroclor analysis compared to congener analysis for CRM samples is consistent with the findings of total PCB concentrations for the split samples, where congener analysis consistently showed higher bias compared to either of the Aroclor analyses (**Figure 1**).

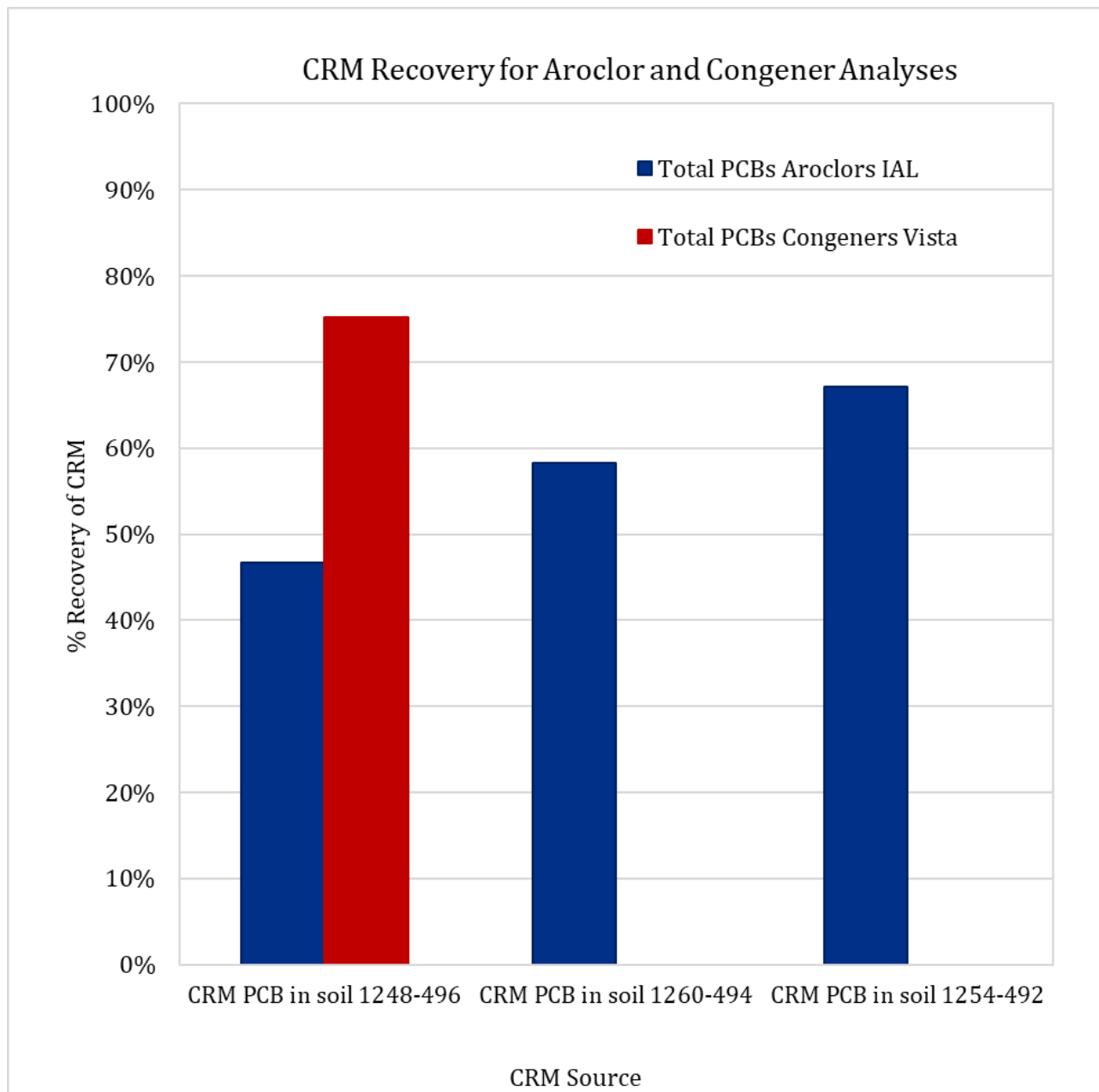


**Figure 1 Total PCB concentrations for Aroclor and Congener analyses**

<sup>1</sup> Human Health Recreational Risk-Based Concentration

<sup>2</sup> Floodplain Preliminary Remediation Goal

<sup>3</sup> Human Health Residential Risk-Based Concentration



**Figure 2 CRM sample recovery for Aroclor and Congener analyses**

## Conclusions and Recommendations

Based on total Aroclor results from both laboratories and the total congener results received for split sampling for OU-5 Area 1:

- identification and quantitation of individual Aroclors by method 8082A is fairly consistent as performed by each laboratory following their own SOPs for extraction and analysis,
- results are biased low for total Aroclor analysis by method 8082A compared to congener analysis by method 1668A,
- method 1668A congener analysis has a better recovery of the CRM sample, Aroclor 1248, compared to Aroclor analysis by method 8082A,
- the congener results for eight of the eleven split sample sets submitted for congener analysis are greater compared to the total PCB concentration reported by Method 8082A,
- the congener results for four of the eleven split sample sets submitted for congener analysis increased the total PCB concentration over the ecological risk value of 11ppm compared to the lower total PCB concentration reported by Pace.

Based on the CRM results and the total PCB by congener analysis, there appears to be low bias across all soil total Aroclor PCB results, regardless of laboratory. Essentially, Aroclor analyses do not appear to be accurately quantifying the total PCB concentration in site soils. These bias impact not only our understanding of the nature and extent of site contamination, but also the associated potential risks to human health and the environment. Consequently, and based on these split sample results, we recommend proceeding with congener analysis in future sampling efforts. The congener analysis procedure was included as a part of the 2016 QAPP, and it is recommended that the established 2016 QAPP is followed in the future sampling events by utilizing congener analysis for quantification of overall PCB contamination.

There are several ways that congener analysis might be applied at this site that do not include running all samples for congener analysis (the items below are not intended to be an exhaustive list of possibilities):

1. Submit select samples for congener analysis:
  - a) Those samples with total Aroclor PCB results approaching within some factor of a site action level.
  - b) Other location specific samples of concern based on historical results or other factors.
2. Submit a suitable portion of the samples collected from the site for total PCB by congener analysis to be used in generating site specific correction factors that can be applied to total PCB by Aroclor results.

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